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Equilibrium Distribution Coefficients for Extraction of Organic Priority Pollutants from Water - II

California Univ., Berkeley

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Robert S. Kerr Environmental Research Lab.
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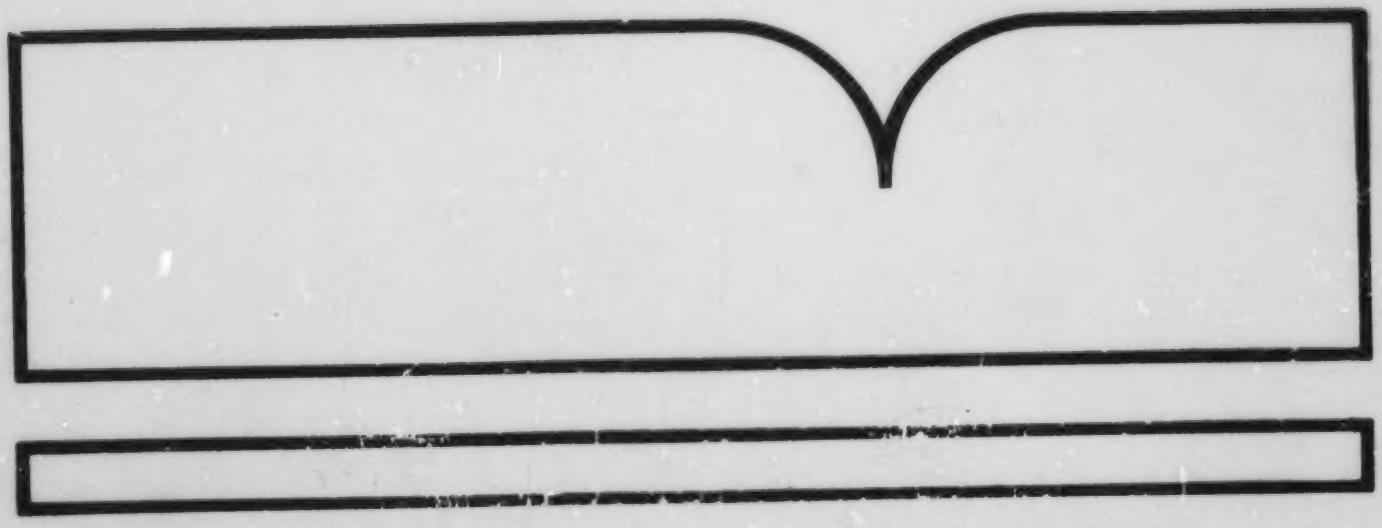

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EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR EXTRACTION OF ORGANIC PRIORITY POLLUTANTS FROM WATER - II

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Equilibrium distribution coefficients have been determined for extraction of acrolein, acrylonitrile, N-nitrosodimethylamine, isophorone, 2-chlorophenol, bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, phenol, resorcinol, pyrogallol, and nitrobenzene from water into a variety of solvents including paraffins, aromatics, ketones, esters, ethers, phosphates, chlorinated hydrocarbons, alcohols, carboxylic acids, and amines. These results are interpreted in terms of Lewis-acid, Lewis-base concepts.

Equilibrium distribution coefficients are also measured for extraction of benzene, toluene, ethylbenzene, chlorobenzene, 1-2 dichloroethane, 1-1-1 trichloroethane, 1-1-2-2 tetrachloroethane, 1-2 dichloropropane, 1-2 transdichloroethylene, trichloroehtylene, tetrachloroethylene, and bromoform from water into undecane, modeling kerosene as a solvent. In all cases, values of distribution coefficient are high enough to make extraction into kerosene an attractive removal process.

Vapor-liquid equilibrium data and results of 72-hour stability tests are reported for mixtures of acrolein or acrylonitrile with several candidate solvents. On the basis of the experimental results likely attractive solvents are identified.

Conceptual process designs and economic analyses are carried out for a number of solvent/solute systems, and result in projected costs (1982 dollars) of $1.10 to $3.20 per m^3 of water for removal of solutes present at 200 to 1000ppm levels in water.

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FOREWORD

The Environmental Protection Agency is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life. In partial response to these mandates, the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, is charged with the mission to manage research programs to investigate the nature, transport, fate, and management of pollutants in ground water and to develop and demonstrate technologies for treating wastewaters with soils and other natural systems for controlling pollution from irrigated crop and animal production agricultural activities; for developing and demonstrating cost-effective land treatment systems for the environmentally safe disposal of soild and hazardous wastes.

This report presents the basic information and procedures for development of solvent extraction techniques to remove a number of the priority pollutants from wastewaters at their source, thereby preventing entry into the environment at diluted levels. Early removal from lower wastewater volumes prevents the risks of broadening the exposure to the pollutants and ameliorates the technical and economic problems associated with cost-effective removal or treatment of low concentrations in large volumes of wastewater.

Volume I presents the data for halogenated hydrocarbons and aromatics, phenols, acrolein, acrylonitrile, and nitrobenzene. Volume II includes additional distribution coefficient data plus conceptual designs and process economics projections.

Clinton W. Hall

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Director
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ABSTRACT

Equilibrium distribution coefficients have been determined for extraction of acrolein, acrylonitrile, N-nitrosodimethylamine, isophorone, 2-chlorophenol, bis(2-chloroethyl)ether, and bis(2-chloroethoxy)methane from water into various solvents. These data supplement similar data given in an earlier report (EPA) for chlorinated hydrocarbons, aromatics, bromoform, phenol, resorcinol, pyrogallol, 2-chlorophenol, 2-nitrophenol, acrolein, acrylonitrile, and nitrobenzene.

Results are presented for vapor-liquid equilibrium measurements for mixtures of acrolein and acrylonitrile with various candidate solvents (methylene chloride; methyl isobutyl ketone; n-butyl acetate; 1,1,2,2-tetrachloroethane; toluene), and for high-temperature 72-hour stability tests with these and other solvents. On the basis of these results recommendations are made (Table 6-1) for particular solvents effective for particular solutes.

Conceptual designs and economic analyses were carried out, giving projected (1982) costs of $4 to $10 per 1000 gallons ($1 to $2.50 per m^3) of water for removal of solutes at the 200 to 1000 ppm level.

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SECTION 1

INTRODUCTION

This report is the second of a series of two reports dealing with the removal of certain of the organic EPA Priority Pollutants from water by means of solvent extraction. The principal focus of the project has been measurement of equilibrium distribution coefficients (equivalent to partition coefficients, or solvent capacities) for extraction of these organic solutes from water by various candidate solvents. The equilibrium distribution coefficient, K_D, is defined as the weight fraction of the solute in the solvent phase divided by the weight fraction of the solute in the aqueous phase, at equilibrium and at high dilution. The first report of the series (King, et al, 1982) is denoted throughout this report as "I". It contains a general discussion of solvent selection, along with equilibrium-distribution-coefficient data for extraction of phenol, resorcinol, pyrogallol, 2-chlorophenol, 2-nitrophenol, acrolein, acrylonitrile, nitrobenzene, aromatic hydrocarbons (benzene, toluene, ethylbenzene), and a variety of halogenated hydrocarbons (chlorobenzene; 1,2-dichlorobenzene; chloroform; carbon tetrachloride; 1,1-dichloroethane; 1,2-dichloroethane; 1,1,1-trichloroethane; 1,1,2,2-tetrachloroethane; 1,2-dichloropropane; 1,2-trans-dichloroethylene; trichloroethylene; tetrachloroethylene; and bromoform). The data for the aromatics and chlorinated hydrocarbons have been summarized in a paper by Barbari & King (1982).

This second report contains data for equilibrium distribution coefficients of N-nitrosodimethylamine, isophorone, bis(2-chloroethyl)ether, and bis(2-chloroethoxy)methane, along with additional data for acrolein, acrylonitrile, and 2-chlorophenol. Also, tests of regenerability and chemical stability at elevated temperature are reported for systems of several solvents with acrolein and acrylonitrile, and results of conceptual designs and economic analyses are reported for cases of nine different extractions, removing acrolein, acrylonitrile, 2-chlorophenol, or nitrobenzene from water using various solvents.

Equilibrium measurements and design studies for the more polar solutes are summarized in a paper by Joshi, et al (1982).

Solvents for study were selected on the basis of several factors, discussed in more detail in I. These include probable chemical stability and regenerability; low solubility in water; lack of toxicity; lack of emulsifying tendencies; low cost; favorable density, viscosity, and interfacial tension; and high K_D. As reported in I, kerosene is an attractive solvent for aromatics and chlorinated hydrocarbons; however, the more polar organics require more polar solvents for effective removal. It is particularly useful to trade upon concepts of Lewis acidity and Lewis basicity (electron acceptors and electron donors), using a basic solvent to extract an acidic solute, and vice versa. A basic or acidic extractant will often be used in conjuction with a diluent, which itself can have a strong effect upon K_D -- often very favorable. Hence mixed solvent systems are of interest. Low-boiling (lower boiling point than the solute) and high-boiling (higher boiling point than

the solute) solvents lead to fundamentally quite different processes. High-boiling solvents ususally lead to substantially less energy consumption, because there is no need to boil the solvent overhead in a distillation-regeneration step. However, high-boiling solvents can experience thermal degradation due to high temperatures in the reboiler of the regenerator, and can suffer from build-up of heavy tars and degradation products. Which will be more attractive depends upon the characteristics of the water stream to be extracted. For that reason, we have, in general, sought to identify at least one attractive low-boiling solvent and at least one attractive high-boiling solvent for each solute.

SECTION 2

CONCLUSIONS

Equilibrium distribution coefficients have been measured for extraction of acrolein, acrylonitrile, N-nitrosodimethylamine, isophorone, 2-chlorophenol, bis(2-chloroethyl)ether, and bis(2-chloroethoxy)methane from water into various solvents. Vapor-liquid equilibrium data pertinent for solvent regeneration by distillation have been measured for mixtures of acrolein and acrylonitrile with various solvents. Seventy-two hour stability tests have been carried out for mixtures of acrolein and acrylonitrile with various solvents, under conditions of refluxing at the atmospheric boiling point and/or heating in a thermostatted bath. Instabilities were monitored through changes in boiling temperature, appearance, and/or ratio of solute to solvent, and through additional gas-chromatograph peaks.

Appropriate low- and high-boiling solvents for these solutes are identified in Section 6, on the bases of equilibrium distribution coefficient, boiling point, solution non-idealities, stability tests, and other standard criteria such as availability, cost, and solubility of the solvent in water. Many of the recommended solvents are Lewis bases -- ketones and tributyl phosphate -- which complex selectively and effectively with many of the solutes in questions, which have Lewis-acid properties.

Conceptual designs and economic analyses have been carried out for a number of combinations of solutes and solvents, giving costs ranging from $4 to $10/1000 gallons of water ($1 to $2.50/$m^3$).

SECTION 3

RECOMMENDATIONS

Solvent extraction should be given more serious consideration as an effective means for removing problem pollutants from water. It has particular advantages where a solute is non-biodegradable or toxic to biotreatment systems, or where the concentration and value of the solute are such that there is economic incentive for recovering the solute. In competition with stripping as a recovery process, extraction has advantages when the solute forms an azeotrope with water (as does phenol), or where very high solvent capacity can lead to a very low steam requirement for solvent regeneration.

In the present work, solvent-stability tests were carried out for only 72 hours, and for only acrolein and acrylonitrile as solvents. Before large-scale installations are built for recovering these and other solutes by extraction, it will be desirable to carry out more protracted solvent-stability tests. Near-complete regeneration and recovery of solvent are important for economic viability of extraction processes for water treatment.

Solvent extraction is worthy of consideration for removal of a variety of polar-organic pollutants from water. Its possibilities extend well beyond the particular solutes considered in this project.

SECTION 4

EQUILIBRIUM DISTRIBUTION COEFFICIENTS

In this section measurements of equilibrium distribution coefficients for various solute/solvent systems are reported. These results supplement those presented previously in I.

Acrolein

Table 4-1 gives measured values of K_D* for extraction of acrolein from water using various solvents. Earlier data obtained in this project for extraction of acrolein are given in Table 7-1 of I. The experimental procedure used is the same as that described for acrolein in I. Exactly one mL of acrolein was added to 200 mL of Milli-Q grade distilled water to make a stock solution containing 4150 ppm w/w acrolein. In each extraction 50 mL of this solution were contacted with 20 mL of solvent, agitated for 25 minutes at 300 rpm in an orbital shaker, and allowed to settle for 1.0 hour. The raffinate was then centifuged for 1.0 hour, and analyses were made of the aqueous feed and the raffinate, using gas chromatography. K_D was computed from these two analyses by the equation

$$K_D = \frac{w_F - w_R}{w_R} \cdot \frac{W}{S} \qquad (4.1)$$

where w_F and w_R are the weight fractions of solute in the aqueous feed and raffinate, respectively, and S and W are the masses of solvent and water, respectively. This equation postulates complete immiscibility of solvent and water.

The relatively high values of K_D for the chlorinated-hydrocarbon solvents stem from their Lewis acidity, which interacts favorably with the electron-rich oxygen in the aldehyde group of acrolein. Tetrachloroethylene is less acidic that the other chlorinated solvents, and gives correspondingly lower values of K_D. Isobutyl heptyl ketone (IBHK), octyl acetate, and isobutyl isobutyrate were examined as solvents having sufficiently low water solubility so that it would probably not be necessary to remove residual dissolved solvent from water. IBHK gives substantially lower K_D than do lower-molecular-weight ketones. Values of K_D reported in I are 4.9 for methyl isobutyl ketone, and 1.6 for diisobutyl ketone.

Values of K_D derived from back-extraction experiments test the reversibility of the extraction. For methylene chloride values of K_D are

---

*K_D = wt. fraction of solute in organic phase, divided by weight fraction of solute in aqueous phase, at equilibrium and (usually), at high dilution.

TABLE 4-1. MEASURED VALUES OF K_D FOR EXTRACTION OF ACROLEIN FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D	
	Individual	Average
Isobutyl heptyl ketone (IBHK)	0.92 0.93	0.93
Methylene chloride	6.85 6.55 6.22 6.67* 6.53 6.79*	6.6
Tetrachloreoethylene	0.55 0.53	0.54
1,2-Dichloroethane	3.75	3.75
1,1,2-Trichloroethane	3.2 3.7	3.45
1,1,2,2-Tetrachloroethane	4.70 4.47	4.6
Diisopropyl ether	1.82 1.62	1.7
Ethyl propionate	1.59 1.49	1.5
n-Octyl acetate	1.76 1.64	1.71
Isobutyl isobutyrate	1.97 1.99	1.98
Nitropropane	3.81 3.55 2.79* 3.63 2.77*	(3.6)

* - Back-extraction of extract from previously listed run.

essentially the same, and certainly no lower, than those for forward extraction, thereby indicating reversibility. For nitropropane, on the other hand, the values of K_D for back-extraction are significantly lower than those for the forward extraction, indicating irreversibility or a kinetic limit. Such behavior makes nitropropane undesirable as a solvent.

The values of K_D for diisopropyl ether are in line with values reported in I for di-n-butyl ether. Much higher values of K_D were inferred from data for unpurified diisopropyl ether, and back-extraction data indicated irreversibility. However, the ether was purified by washing with ferrous sulfate solution until a KI test proved negative; this brought the indicated K_D values down to the level reported in Table 1. Presumably, the presence of small amounts of peroxide impurities greatly enhances extraction, but in an irreversible manner.

Data are reported in Table 4-2 for the effect of feed concentration on the measured values of K_D for acrolein into various solvents. In the case of butyl acetate, higher aqueous feed concentration appears to enhance K_D.

Acrylonitrile

Table 4-3 reports measured values of K_D for extraction of acrylonitrile into various solvents, beyond the values reported in Table 8-1 of I. The procedure was the same as that described in I for acrylonitrile, with an aqueous feed concentration of 3200 ppm w/w.

The effectiveness of the chlorinated hydrocarbons as Lewis acid solvents is apparent from the results for methylene chloride and tetrachloroethane, as well as from the value of $K_D = 6.5$ reported for chloroform in I. The first two values reported for methylene chloride apparently reflect gross directional error. The esters and ketones give attractively high values of K_D, acting as Lewis base solvents, although there is scatter and perhaps irreversibility in the new data taken for MIBK. (Two points reported in I give K_D for MIBK = 7.2 and 6.50). The ethers are weaker bases and give somewhat lower K_D. From these results, it can be seen that acrylonitrile exhibits both acidic and basic properties, and interacts appreciably with solvents of either nature.

The value of K_D for styrene (4.1) is comparable to the value (3.5) reported for toluene in I. The furan gives a value of K_D comparable to the other strong Lewis bases. Tributyl phosphate in various mixtures gives substantial values of K_D, acting as a strong Lewis base. The phosphoric acid gives lower values, perhaps because of dimerization of the acid in the solvent phase.

Table 4-4 reports effects of aqueous feed concentration.

N-Nitrosodimethylamine

Previously reported data for extraction of n-nitrosodimethylamine (NNDMA) from water are shown in Table 4-5. These results are consistent with the

TABLE 4-2. EFFECT OF AQUEOUS FEED CONCENTRATION ON K_D FOR EXTRACTION OF ACROLEIN FROM WATER

Solvent	K_D	
	4150 ppm Feed	91500 ppm Feed
n-Butyl acetate	2.38	4.31
	2.75	4.21
1,1,2,2-Tetrachloroethane	4.70	4.43
	4.47	3.90
Methyl isobutyl ketone (MIBK)	4.90	3.50
	4.91	2.90
	4.84	
Toluene	2.05	2.02
	2.25	

TABLE 4-3. MEASURED VALUES OF K_D FOR EXTRACTION OF ACRYLONITRILE FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D Individual	Measured K_D Average
Methylene Chloride	13.4 13.5 7.7 7.6* 9.3 8.7* 8.9 8.3	8.6
1,1,2,2-Tetrachloroethane	7.2 7.2	7.2
n-Butyl Acetate	5.2 5.6	5.4
Isobutyl Isobutyrate	3.3 3.7	3.5
n-Butyl Ether	3.3 3.1	3.2
Diisopropyl Ether	2.53 2.61	2.6
Methyl Isobutyl Ketone (MIBK)	5.7 4.5* 6.4 4.9*	(6.1)
Isobutyl Heptyl Ketone (IBHK)	1.29 1.16	1.2
Styrene	4.2 3.95	4.1
2-Methyl Furan (99% purity)	3.8 4.2	4.0
Tricresyl phosphate	2.70 2.67	2.7

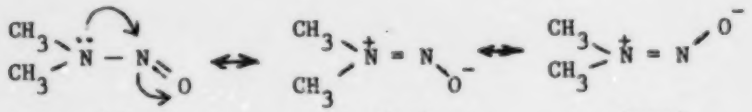
TABLE 4-3 (Continued)

50% Tributyl Phosphate (TBP): 50% undecane v/v	3.42 3.54	3.5
25% TBP: 75% Diisobutyl Ketone (DIBK) v/v	4.03 3.90	3.96
50% TBP; 50% DIBK v/v	4.18 4.32	4.25
50% Di-2-ethylhexyl Phosphoric Acid (D2EHPA)	1.52 1.27	1.4
50% D2EHPA; 50% TBP v/v	2.77 2.48	2.6

---

* - Back-extraction of extract from previously listed run.

concept that Lewis acids are effective solvents for extraction of NNDMA. This can be rationalized by recognizing that there is a significant charge separation in the resonance hybrid of NNDMA, as shown below:



(I) (II) (III)

The configurational isomers II and III exist due to the high barrier to rotation about the N=N bond. The relative polarizations indicate that hydrogen bonding and complexes with electrophiles would occur at the oxygen atom, while hydrogen bonding and complexes with nucleophiles would occur at the nitrogen atom. However, steric hindrance associated with the electropositive nitrogen would make electrophile attack at the oxygen more likely, thereby rationalizing the higher K_D values for the Lewis acids (methylene chloride and the acids).

NNDMA is on the list of OSHA-regulated known carcinogens. Hence special handling procedures were followed. The bottle of pure NNDMA was stored in a glove box fitted with an activated charcoal scrubber. Dilutions were also made in this glove box. The dilute feed solution containing 400 ppm NNDMA was transferred to an adequately ventilated fume hood using plastic containers and secondary containers to avoid chances of spillage and breakage during transfer. Disposable gloves and lab coats were used. The dilute solution remained in the fume hood during the entire period of extraction and analysis. The shaker, centrifuge and liquid chromatograph were also kept inside the fume hood. Liquid wastes generated during the experiments, including the contaiminated carrier solvents from HPLC operations, were collected in bottles and disposed of by the Environmental Health and Safety Department of the University. Inactivation of NNMDA was accomplished by treating the wastes with 30% HBr in glacial acetic acid.

Feed and raffinate samples were analyzed by high-pressure, reverse-phase liquid chromatography, using a nonpolar stationary phase and a polar mobile phase. The mobile phase was fifty volume percent methanol in water. The column was 3.9-mm dia meter X 30-cm long and was packed with $C_{18}H_{37}$ bonded to silica particles (C_{18} μ-Bondapak). The apparatus included a Spectra Physics Model 740 pump and a Waters Associates Model 440 UV absorbance detector, set at 254 nm. The carrier solvent flow rate was 1.0 mL/min., and the residence time for the nitrosodimethylamine peak was about 3.3 minutes. A Hewlett Packard Model 3390A digital integrator was used.

NNDMA is not a commerical chemical. It occurs in the environment because of reactions between its precursors -- nitrates or nitrogen oxides and amines. Hence the expected concentration for NNDMA in any wastewater stream is quite low, probably at ppb levels. The synthetic feed chosen for the present work contained a much higher concentration of NNDMA, 400 ppm, so as to allow for easier detection and better reproducibility. The calibration curve for NNDMA concentration vs. peak area was found to be linear up to 1000 ppm.

TABLE 4-4. EFFECT OF AQUEOUS FEED CONCENTRATION ON K_D FOR EXTRACTION OF ACRYLONITRILE FROM WATER

Solvent	K_D 3200 ppm Feed	K_D 34,600 ppm Feed
Methylene Chloride	(8.6)	10.9 10.3
50% TBP; 50% Undecane v/v	3.5	3.9 3.25
1,1,2,2-Tetrachloroethane	7.2	6.3 5.5
50% Adogen 283; 50% Undecane v/v	—	0.11 0.28

TABLE 4-5. PREVIOUSLY REPORTED VALUES OF K_D FOR EXTRACTION OF N-NITROSODIMETHYLAMINE FROM WATER

Solvent	K_D	Reference
1-octanol	1.06	(1)
Methylene chloride	3.8	(2)
Diethyl ether	0.28	(2)

1. Radding, (1977)
2. Issenberg, (1977)

TABLE 4-6. MEASURED VALUES OF K_D FOR EXTRACTION OF N-NITROSODIMETHYLAMINE FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D Individual	Measured K_D Average
2-Octanol	0.34 0.28	0.31
1-Octanol	0.35 0.32	0.34
2-Ethylhexanol	0.44 0.23	(0.3)
2-Ethylhexanoic Acid	0.45 0.39	0.42
Toluene	0.75 0.60	0.68
50% D2EHPA; 50% Undecane v/v	0.43 0.42	0.43
Methyl Isobutyl Ketone (MIBK)	0.69 0.57	0.63
Isobutyl Heptyl Ketone (IBHK)	0.20 0.07	
Methylene Chloride	2.56, 2.40* 2.64, 2.48* 2.58, 2.30* 2.59, 2.42* 2.68, 2.55* 2.46, 2.39*	2.59
Dichlorobenzene (1,2)	0.64 0.54	0.59
14% Trioctylphosphine Oxide (TOPO); 86% IBHK w/w	0.21	
50% TBP; 50% Decalin	0.37	0.3

TABLE 4-6 (Continued)

(Decahydronaphthalene) v/v	0.25	
n-Butyl Acetate	0.65 0.51	0.6
Diisopropyl Ether	0.23 0.30	0.27
50% Adogen 283; 50% 2-Ethyl-hexanol v/v	0.20 0.27	0.24
50% Adogen 364; 50% 2-Ethyl-hexanol v/v	0.29 0.30	0.30

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* - Back extraction of extract from previously listed run.

Extractions were carried out in duplicate, each run with 50 mL feed and 20 mL solvent. The mixture was agitated for 25 minutes at 300 rpm using an orbital shaker, unless otherwise indicated. The mixture was allowed to settle for one hour before analysis.

NNDMA is known to undergo photolysis under acidic conditions but should be stable at neutral or alkaline pH. Although our feed solution is neutral, all the containers and centrifuge tubes were covered by black tape to eliminate any chances of photolysis. Analysis of the feed at the beginning and at the end of a run did not show any instability.

Experimentally measured values of apparent equilibrium distribution coefficents (K_D) from these runs are reported in Table 4-6. Some of the earlier values given in the June 1982 progress report were in error because of the way the digital integrator was operated for low peak areas. The values of K_D given in Table 4-6 are free of that source of error. It should be noted that the data for methylene chloride and 1-octanol differ from the values reported by Radding, et al (1977) and Issenberg (1977).

In reviewing the data in Table 4-6, it can be seen that the values of K_D are in general quite low, consistent with the high water solubility and very polar nature of NNDMA. The highest value of K_D, by far, is shown by methylene chloride, probably acting as a Lewis acid. The data for back-extraction from methylene chloride are all somewhat lower than the data for forward extraction, by an average of 6%. This may represent some irreversibility or kinetic effect, but more like it represents either the effect of an impurity in the methylene chloride, or else an effect of concentration level on K_D.

Other solvents giving values of K_D of 0.5 or higher are the aromatics (toluene, dichlorobenzene), MIBK and butyl acetate. The latter two solvents are Lewis bases, and would interact with the Lewis-acid properties of NNDMA. It is possible that mixtures of Lewis-acid and Lewis-base solvents might be effective, but this was not explored further.

Isophorone

Isophorone, along with acrolein, falls in the category of α,β-unsaturated carbonyl compounds. In such compounds there is a delocalization of the olefinic electrons, which can result in the compounds having both electron-donor and electron-acceptor properties. The results shown in Table 4-7 were obtained by the usual experimental techniques, with aqueous-feed concentration ranging from 462 to 923 ppm w/w, with solvent/aqueous feed ratios ranging from 0.10 to 0.20 v/v, and with analysis of aqueous phases carried out by gas chromotography. These results show positive effects of both Lewis-acid and Lewis-base solvents. Values of K_D are generally high, because of the low solubility of isophorone in water, 1.2 wt% (Union Carbide, 1978). More information on these experiments and their interpretation is given by Senetar (1982).

Figures 4-1, 4-2, and 4-3 show results of measurements of K_D for solvent mixtures containing one of four different extractants (TBP, neodecanoic acid, D2EHPA, DIBK) in one of three different diluents (undecane, DIBK, toluene).

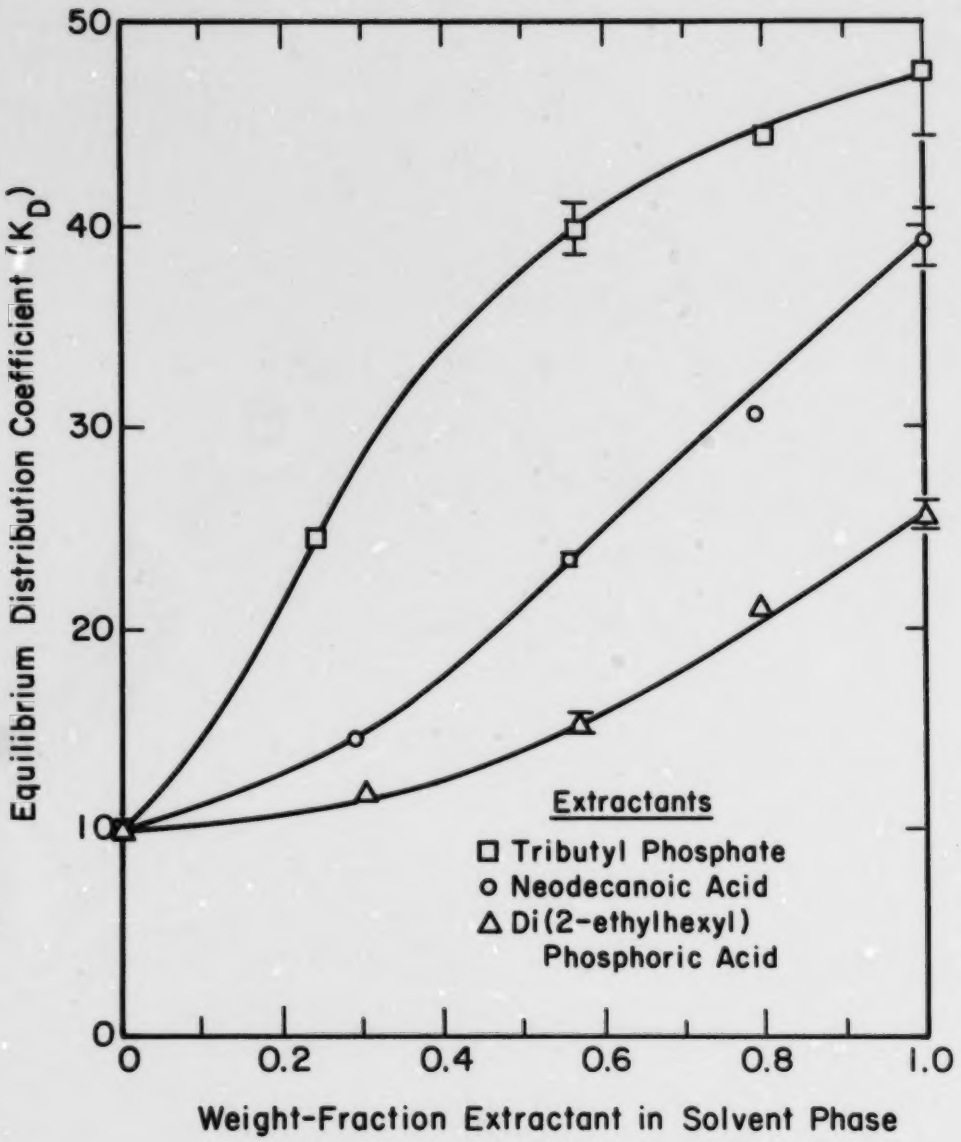


Figure 4-1. Equilibrium distribution coefficient (K_D) versus weight-fraction extractant for extraction of isophorone from water with undecane as a diluent.

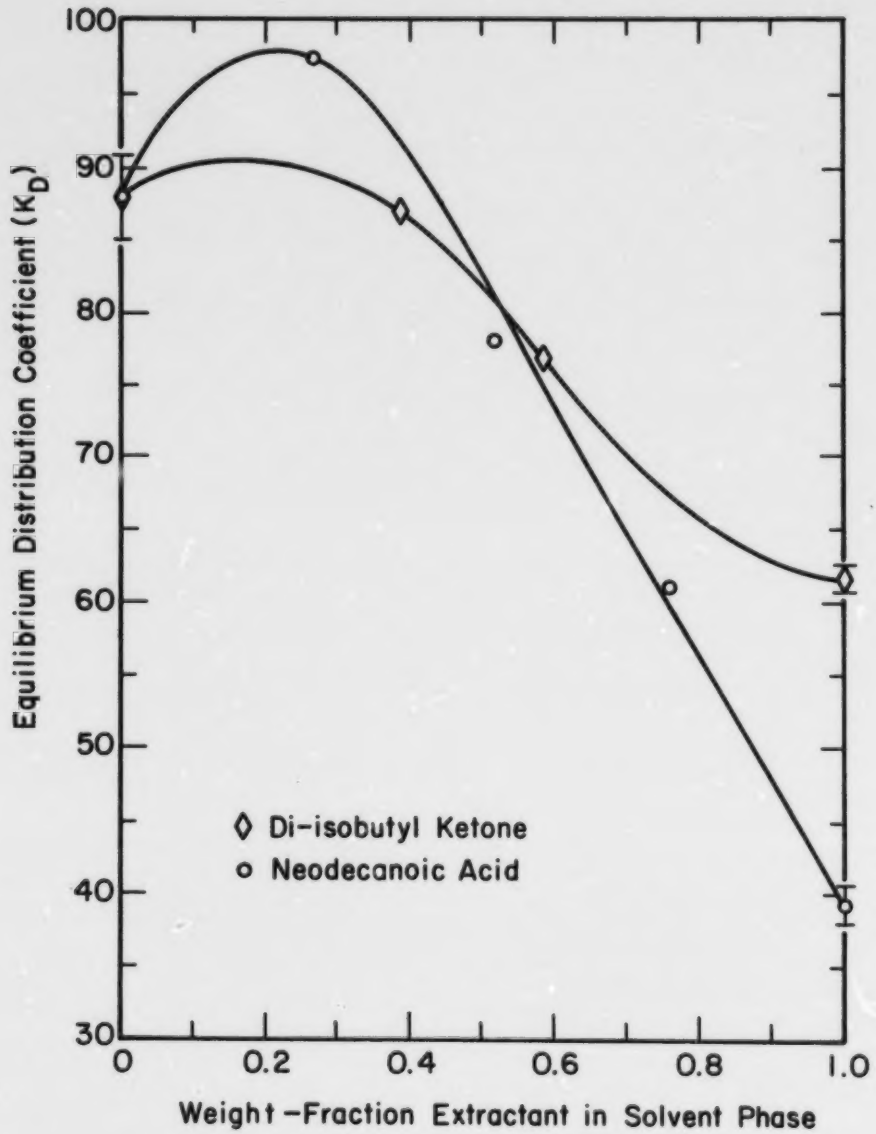


Figure 4-2. Equilibrium distribution coefficient (K_D) versus weight-fraction extractant for extraction of isophorone from water with di-isobutyl ketone as a diluent.

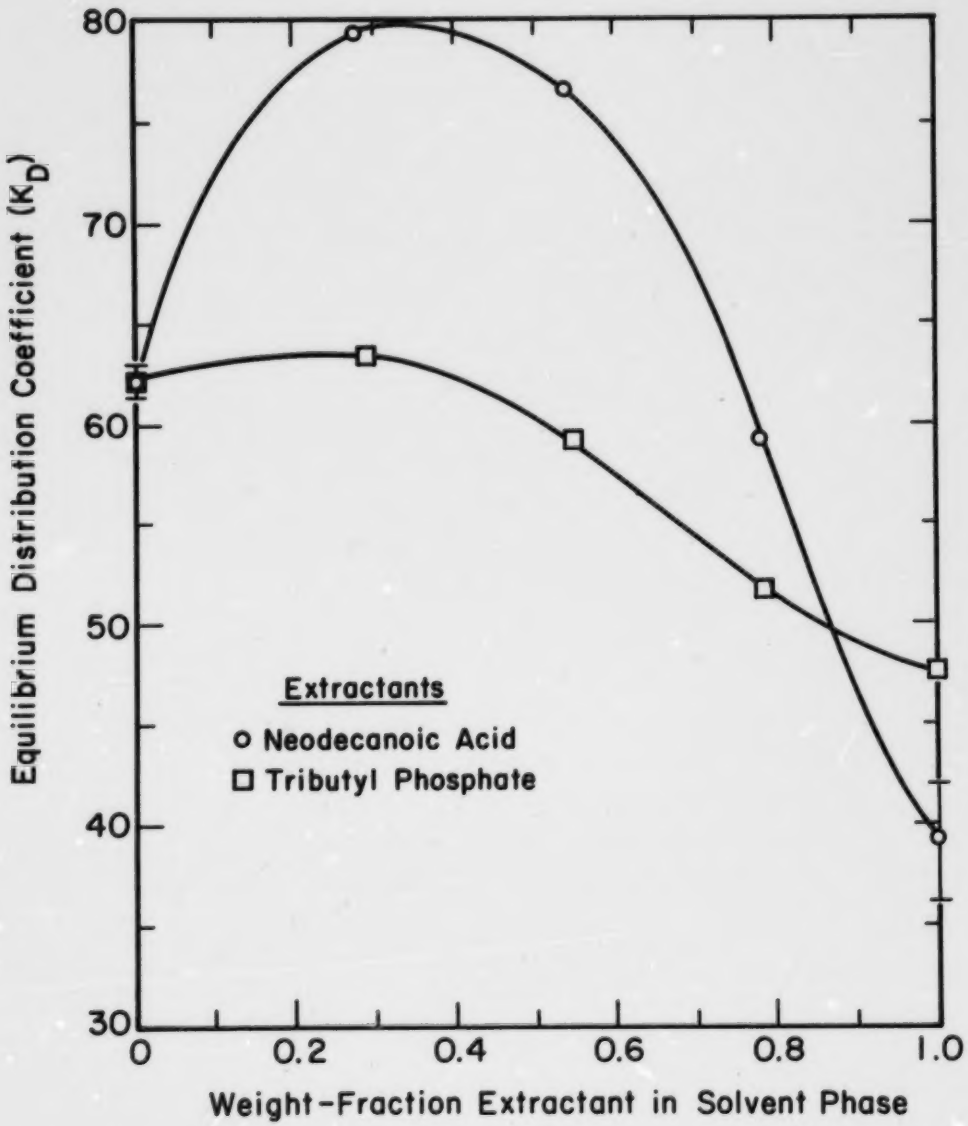


Figure 4-3. Equilibrium distribution coefficient (K_D) versus weight-fraction extractant for extraction of isophorone from water with toluene as a diluent.

Here it can be seen that in some cases, notably neodecanoic acid/DIBK and neodecanoic acid/toluene, a synergism exists such that K_D for an intermediate solvent composition is greater than that for either solvent constituent alone. This can result from any of several factors -- (1) simultaneous interaction of Lewis-acid and Lewis-base solvent components with different base and acid substituent groups on the solute; (2) enhancement of the basicity of the oxygen atom in the carboxylic acid, by virtue of the Lewis-base diluent; and/or (3) breaking apart dimers of the carboxylic acid because of preferential interaction with a basic solvent diluent.

2-Chlorophenol

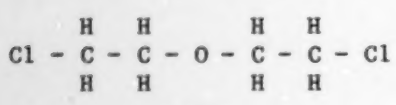
Values of K_D for extraction of 2-chlorophenol into undecane (about 11) and tricresyl phosphate (about 1000) are reported in I. Like other phenols, 2-chlorophenol is a Lewis acid, made stronger by the effect of the chlorine substituent. Hence additional K_D measurements were made with Lewis-base solvents -- several ketones and another phosphate. Aqueous feed concentrations of 995 and 1990 ppm w/w were used, along with solvent/water volumetric phase ratios ranging from 0.05 to 0.20. Analyses of aqueous feed and raffinate phases were made by gas chromatography. More details are given by Senetar (1982).

Experimental results are reported in Table 4-8. The ketones give quite high values of K_D, decreasing with increasing ketone molecular weight because of the lesser density of carbonyl functional groups. The phosphate, TBP, is a stronger base, and therefore gives still higher K_D. TBP gives a value of K_D higher than that reported in I for TCP, both because of the higher molecular weight of TCP and because the presence of the phenyl substituents on TCP makes it a less strong base than the alkyl substituted TBP.

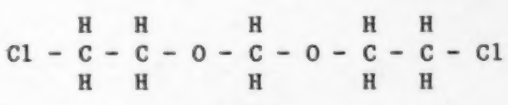
Chlorinated Ethers

Measurements were made for two of the chlorinated ethers on the EPA Priority Pollutant list -- bis(2-chloroethyl) ether and bis(2-chloroethoxy) methane, denoted b2CEE and b2CEM respectively.

These two compounds have the structures indicated below:



b2CEE



b2CEM

The ether oxygens have weakly basic character, but the stronger effect should be Lewis acidity of the hydrogen atoms on the electronegative chlorines on the same atoms. In addition, b2CEM should have acidic hydrogens on the central carbon atom, resulting from the presence of the two adjacent atoms. One would therefore expect Lewis-base solvents to be the most effective, with b2CEM giving higher values of K_D with such solvents than does b2CEE.

Table 4-9 reports results of measurements with these two ethers, with aqueous feed concentrations of 1200 or 2400 ppm w/w, volumetric solvent/water phase ratios of 0.10 or 0.20, and analyses of aqueous feed and raffinate phases by gas chromatography. Details of these experiments are given by Senetar (1982). The values of K_D with the basic solvents are substantially greater than those with undecane, as expected. K_D increases with decreasing

TABLE 4-7. MEASURED VALUES OF K_D FOR EXTRACTION OF ISOPHORONE FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D Individual	Average
Undecane	10.9	
	10.5	
	9.9; 10.4*	10.2
	9.6; 10.7*	
Toluene	85	
	92; 95*88	
	87	
Methyl Isobutyl Ketone (MIBK)	93	
	106 98	
	95; 91*	
Diisobutyl Ketone (DIBK)	62	62
	64	
	61	
Neodecanoic Acid	41	
	39; 39*	39
	38; 37*	
Tributyl Phosphate (TBP)	54	
	48	
	48; 49*	
	44	48
	43	
	45; 46*	
Di-2-ethylhexyl Phosphoric Acid (D2EHPA)	25	
	24	
	27; 25*	26
	27; 26*	

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* - Back-extraction of extract from previously listed run.

TABLE 4-8. MEASURED VALUES OF K_D FOR EXTRACTION OF 2-CHLOROPHENOL FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D Individual	Average
Methyl Isobutyl Ketone (MIBK)	570	
	580; 580*	600
	640	
Diisobutyl Ketone (DIBK)	320; 340*	
	380	370
	395	
Isobutyl Heptyl Ketone (IBHK)	161	
	160	
	158; 147*	159
	158; 145*	
Tributyl Phosphate (TBP)	2570	
	2510	
	2640	2700
	2620; 2130*	
	2940; 2940*	

* - Back extraction of extract from previously listed run. These have not been included the average.

TABLE 4-9. MEASURED VALUES OF K_D FOR EXTRACTION OF BIS(2-CHLOROETHYL) ETHER AND BIS(2-CHLOROETHOXY) METHANE FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D bis(2-chloroethyl) ether		bis(2-chloroethoxy) methane	
	Individual	Average	Individual	Average
Undecane	11.5 10.6 10.9 11.0	11.0	12.0 12.6 12.3 12.5	12.4
Methyl Isobutyl Ketone (MIBK)	120 119 115 114	117		
Diisobutyl Ketone (DIBK)	71 68 70; 68* 70; 67*	70	112 110; 112* 125; 117*	116
Isobutyl Heptyl Ketone (IBHK)	51 50 50; 49* 50; 50*	50		
Tributyl Phosphate (TBP)	84 84 81; 84* 85; 86*	83	123 129 84; 84* 84; 86*	

* - Back extraction of extract from previously listed run.

solvent molecular weight for the ketone solvents, because of the greater density of basic functional groups. Despite the high molecular weight, IBHK remains a surprisingly good solvent for b2CEE. TBP gives K_D not much different from the ketones -- a result of the higher molecular weight of TBP offsetting its stronger basicity.

SECTION 5

SOLVENT REGENERABILITY AND STABILITY

Measurements of Vapor-Liquid Equilibrium

Solvent regeneration would most likely be accomplished by distillation. It is therefore important for a solvent to have a relative volatility with respect to the extracted solute that is sufficiently different from 1.0 across the entire composition range. There have not been previous experimental measurements of vapor-liquid equilibrium (VLE) data for most of the solute/solvent systems of interest.

A vapor-recirculating equilibrium still manufactured by Cal-Glass was used to measure VLE for mixtures of acrolein or acrylonitrile with various promising solvents. The principle of the still is described by Hipkin and Myers (1954). A check was made of the performance of the still, using the n-heptane/toluene system, for which reliable literature data are available. For a liquid phase containg 42.7 mole percent heptane, the equilibrium vapor at 1 atm and 102°C contained 51.8 mole % heptane, giving a relative volatility of 1.43. The results compares favorably with the value of 1.45 reported by Hipkin and Myers (1954).

Table 5-1 reports VLE data for mixtures of acrolein with several different solvents. From the vapor- and liquid-phase mole fractions, y and x, respectively, the relative volatility α_{ij}, where i is acrolein and j is the solvent, is calculated as

$$\alpha_{ij} = \frac{y_i}{x_j} \quad \frac{x_j}{y_i} \tag{5-1}$$

The activity coefficient of acrolein, γ_i, is calculated from the measured mole fractions, the vapor pressure of acrolein (P_i^o) at the measured temperature, and the total pressure (P), which was 1.0 atm in all cases except for MIBK, for which the pressure was 0.79 atm.

$$\gamma_i = \frac{y_i}{x_i} \quad \frac{P}{P_i^o} \tag{5-2}$$

For an ideal solution, $\gamma_i = 1.0$. If residual complexation between acrolein and the solvent exists at the distillation temperature, then γ_i can be less than 1.0. If the effects of positive deviations from ideality outweigh complexation effects, γ_i can be greater than unity.

TABLE 5-1. VAPOR-LIQUID EQUILIBRIUM FOR ACROLEIN-SOLVENT MIXTURES

Solvent	Temp (°C)	Mole Fraction of Acrolein		Relative Volatility of Acrolein with Respect to Solvent	Activity Coefficient of Acrolein
		Liquid Phase	Vapor Phase		
Methylene Chloride	42.7	0.0922	0.0464	0.48	0.74
	48.0	0.5290	0.4640	0.78	1.03
	51.2	0.8340	0.7960	0.77	1.00
Methyl Isobutyl Ketone (MIBK)	100.2	0.0242	0.0995	4.50	0.80
	94.1	0.0425	0.2176	6.30	1.16
	50.9	0.8085	0.9575	5.40	1.00
n-Butyl Acetate	77.7	0.3695	0.8533	10.10	1.05
	100.3	0.1399	0.5941	8.99	1.04
1,1,2,2-Tetrachloro-ethane	121.6	0.1011	0.5483	10.79	0.80
Toluene	78.0	0.260	0.717	7.21	1.24
	85.0	0.169	0.616	7.91	1.34

TABLE 5-2. VAPOR-LIQUID EQUILIBRIUM FOR ACRYLONITRILE-SOLVENT MIXTURES

Solvent	Temp (°C)	Mole Fraction of Acrylonitrils: Liquid Phase	Mole Fraction of Acrylonitrils: Vapor Phase	Relative Volatility of Acrylonitril with Respect to Solvent	Activity Coefficient of Acrylontril
Methylene Chloride	41.8	0.0955	0.0391	0.306	1.425
	57.3	0.6154	0.2970	0.265	0.926
	66.9	0.8408	0.6377	0.333	1.035
1,1,2-2-Tetra-chloroethane	129.2	0.1175	0.4735	6.754	1.048
n-Butyl acetate	79.4	0.8896	0.9676	3.64	1.027
	86.7	0.6989	0.8945	3.65	0.972
	110.1	0.1855	0.4952	4.31	1.074
Methyl Isobutyl Ketone (MIBK)	104.0	0.1844	0.4205	3.21	

Methylene chloride is the one low-boiling solvent considered in Table 5-1. It gives an adequate relative volatility with respect to acrolein at low acrolein concentrations, but the mixture becomes more close boiling than desirable at higher acrolein mole fractions. A very large distillation column would be required to give high acrolein purity and high solvent recovery. The other solvents are all high-boiling and give relative volatilities that would lead to relatively simple distillation columns. The derived activity coefficients for acrolein are reasonable in all cases.

Table 5-2 reports similar data for mixtures of acrylonitrile with various candidate solvents, with all data being obtained at atmospheric pressure. Methylene chloride, the low-boiling solvent, is sufficiently more volatile than acrylonitrile so that distillation could be used for regeneration without an undue economic penalty. The other solvents are high-boiling and are adequately removed from acrylonitrile in volatility. Again, the derived values of the acrylonitrile activity coefficient are reasonable.

Stability Tests - Acrolein

Stability tests were carried out, which involved heating mixtures of acrolein and different candidate solvents for protracted periods of time. Table 5-3 (Conditions A, B and C) presents a summary of results of tests where mixtures containing 15-20% v/v acrolein were distilled at total reflux and atmospheric pressure for 72 hours. Glass joints of the distillation apparatus were greased and a cold-finger condenser was used in the vent line to prevent loss. Observations were made of changes in appearance, changes in boiling point, changes in composition (ratio of acrolein peak area to solvent peak area in a gas-chromatographic analysis), and the appearance of extra peaks on the chromatrogram. No extra peaks were ever observed. For Condition D in Table 5-3 the liquid mixtures was held for 72 hours in a thermostatted water bath at 65°C (149°F).

Under Condition A with n-butyl acetate a white solid was formed and the peak-area ratio evidenced substantial disappearance of acrolein. Possible explanations included (1) polymerization of acrolein in the presence of the weakly basic ester, and (2) a Claisen condensation reaction between acrolein and the ester. Further experiments were carried out to distinguish between these causes.

The solid was centrifuged from the solvent mixture, was rinsed several times with water, and was dried in an oven at 90°C for 48 hours. Analysis of the dried solid gave 59.5% carbon, 7.0% hydrogen, and (by difference) 33.5% oxygen. The C/H ratio is 8.45, as compared with predicted ratios of 6.75 and 9.0 for the condensation product and the polymer, respectively. For a cross-linked polymer with the structure given in Vol. 1, p. 260 of the 2nd Edition of the Kirk-Othmer Encyclopedia of Chemical Technology, the predicted C/H ratio is 8.5. Thus the promixate analysis indicates that the solid is a polymer of acrolein.

Several other observations support this conclusion. The acrolein polymer is reported to be fine, white powder, which corresponds to the appearance of the solid. The acrolein polymer is reported to be insoluble in most common

solvents, but dissolves in an aqueous solution of $NaHSO_3$. The white solid was insoluble in MIBK, methylene chloride, and acetone. It dissolved in aqueous $NaHSO_3$ solution in less than an hour at 70°C, and overnight at room temperature. Acrolein polymer darkens upon heating but does not melt (Smith, 1962). This observation was borne out by placing some of the white solid on a plate heated by a Bunsen burner.

Acrolein is known to polymerize in the presence of light and oxygen, and the polymerization is promoted by high temperature and alkaline conditions. It can be slowed by lowering the temperature and/or by adding an inhibitor, such a hydroquinone. The utility of these two approaches for reducing polymerization was explored experimentally.

The acrolein normally used was a reagent-grade sample (Aldrich Chemical Co.) reported to contain 97% acrolein and 200 ppm hydroquinone. The mixture for the stability test was prepared by adding 60 mL of this acrolein to 300 mL of n-butyl acetate, along with 3.037 g hydroquinone. This yielded a hydroquinone concentration of 9600 ppm in the mixture. At the end of the test, the mixture was clear, with no evident solids formation or change in volume. Gas-chromatographic analysis showed little change in the ratio of peak areas between acrolein and butyl acetate.

A stability test was run at lower temperature whereupon the solution turned slightly cloudy. The lower temperature promoted stability but did not eliminate polymer formation altogether.

Formation of the polymer can cause serious operating problems. Reboiler heat-transfer surfaces may become coated with the polymer. These could perhaps be cleaned periodically with hot aqueous solutions of $NaHSO_3$. The formation rate could be lessened by carrying out solvent regeneration as a vacuum distillation. Another approach would be addition of hydroquinone as an inhibitor. This approach is used in commerical production of acrolein, wherein water is full recycled. However, in a water clean-up process hydroquinone would remain in the regenerated solvent and would then be leached out into the water passing through the extractor. K_D for extraction of hydroquinone from water by n-butyl acetate is only 7.2, as is reported by Luecke (1980).

Another way in which butyl acetate might be unsatisfactory as a solvent could be excessive solvent loss due to hydrolysis. To assess whether this would be a problem, extracts from several extractions were collected and boiled at atmospheric pressure and total reflux for 24 hours. Gas-chromatographic analysis of the resulting solutions showed no new peaks.

A similar white solid was observed in the stability tests carried out with acrolein in MIBK solvent. Qualitative tests indicated that this, too, was acrolein polymer. Acrolein polymer was also observed to form during VLE measurements (atmospheric pressure) which were attempted using DIBK as solvent with acrolein.

Tests with MIBK at the lower temperature and with addition of more hydroquinone showed that both these avenues serve to reduce tendencies for acrolein polymerization.

With 1,1,2,2-tetrachloroethane a particularly severe polymerization reaction was noted during refluxing under atmospheric-distillation conditions. The temperature sensitivity seems to be particularly strong in this case, however, since the water-bath test gave no evidence of polymerization.

TABLE 5-3. RESULTS OF STABILITY TESTS FOR MIXTURES OF ACROLEIN AND VARIOUS SOLVENTS. WITH AND WITHOUT HYDROQUINONE STABILIZER, AT DIFFERENT TEMPERATURES

Solvent	Condition*	Temperature (°F)		Peak-Area Ratio		Appearance	Comment
		Initial	Final	Initial	Final		
Isooctane	A	140.0	141.7	0.069	0.068	Clear	Good Balance
n-Butyl Acetate	A	195.0	201.0	0.155	0.108	Opaque White Solid	Acrolein Polymer
	B	183.6	187.6	0.214	0.203	Clear	
	D	149.0		0.209	0.217	Slightly Cloudy	
Methyl Isobutyl Ketone (MIBK)	A	167.0	173.0	0.239	0.172	Opaque White Solid	Acrolein Polymer
	C	179.7	181.5	0.237	0.224	Slightly Cloudy	
	D	149.0		0.238	0.234	Clear	
1,1,2,2-Tetra chloroethane	A	187.7	213.4	0.188	0.000	Opaque White	Acrolein Polymer
	D	149.0		0.238	0.238	Clear	

* Condition: A = Atmospheric-pressure boiling point
B = 9600 pp w/w hydroquinone
C = 1100 ppm w/w hydroquinone
D = Thermostatted water bath

Stability Tests - Acrylonitrile

Similar stability tests were carried out for mixtures of 15-20% acrylonitrile v/v with various solvents. The results are summarized in Table 5-4. In the cases of MIBK, n-butyl acetate, and toluene, a yellowish solid formed in substantial quantities. A literature survey revealed that a cyanoethylation reaction takes place between ketones and acrylonitrile in the presence of basic catalysts (Bruson & Riener, 1942):

$CH_3COCH_2CH(CH_3)_2 + CH_2CHCN \rightarrow CH_3CO(CH_2CH_2CN)_2$

MIBK — acrylonitrile — 4 acetyl-4-isopropyl heptane dinitrile
melting point = 101 C

Probably the same reaction takes place thermally at the atmospheric boiling point. Similar reactions appear to occur with butyl acetate and toluene.

In the case of butyl ether, the solution turned milky white and there was a substantial disappearance of acrylonitrile. Therefore regeneration does not appear to be possible for ethers either.

Tributyl phosphate and the chlorinated hydrocarbons seem to undergo no reactions under regeneration conditions.

TABLE 5-4. RESULTS OF STABILITY TESTS FOR MIXTURES OF ACRYLONITRILE AND VARIOUS SOLVENTS

Solvent	Condition*	Temperature (°F)		Peak-Area Ratio		Appearance	Comments
		Initial	Final	Initial	Final		
MIBK	A	219				Yellow Solid	Cyanoethylation
n-Butyl Acetate	B	215.4	221	0.193	0.184	Yellow Solid	Cyanoethylation
Methylene Chloride	C	109.9	110.2	0.464	0.455	Clear	
50% Tributyl Phosphate 50% Undecane v/v	C	210.9	212.7	0.419	0.416	Clear	
di-n-Butyl Ether	C	192	196.7	0.165	0.129	Milky White	Reaction unknown
Toluene	C	187.6	190.6**	1.1026	0.0986	Yellow-brown resin; volume decrease	Cyanoethylation
1,1,2-2-Tetrachloroethane	C	215.4	216.0	0.789	0.777	Small char-like residue	

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* - Conditions: A = Attempted VLE measurement in Cal-Glass still
B = Refluxed distillation, atmospheric pressure, 48 hours
C = Refluxed distillation, atmospheric pressure, 72 hours

** - Temperature returned to 187.6°F later in test

SECTION 6

SOLVENT SELECTION

Table 6-1 summarizes recommended solvents, based upon the work accomplished in this project. Selection criteria, in addition to availability, cost, etc., include (1) value of K_D, (2) relative volatility between solute and solvent, and (3) stability under regeneration conditions. Where there is some question about a solute, it is placed in parentheses. Recommendations are included for solutes considered in I, as well as those covered in this report.

For many of the solvents (methylene chloride and the lighter ketones, ethers, and esters), the solubility of the solvent in water is high enough so that it is necessary for economic reasons to provide a means of recovering residual dissolved solvent from the effluent water. Alternatives for this include extraction with a non-polar solvent (e.g., an alkane), atmospheric steam stripping, vacuum steam stripping, and inert-gas stripping (Greminger, et al, 1982).

In cases where chlorinated hydrocarbons are recommended, no other common solvent appears to be suitable. The chlorinated hydrocarbons themselves pose environmental problems, and must therefore be thoroughly removed from any released water stream. The alternatives for accomplishing this are the same as those mentioned for solvent recovery in general, with the addition of carbon adsorption.

TABLE 6-1. SOLVENTS RECOMMENDED ON THE BASIS OF WORK IN THIS PROJECT*

Solute	Recommended Solvents	
	Low-Boiling	High-Boiling
Acrolein (53)	--	n-Butyl Acetate * (126) MIBK* (117) tetrachloroethane* (146) Toluene* (111)
Acrylonitrile (78)	Methylene Chloride (40)	TBP (289) + Hydrocarbon (Tetrachloroethane) (146)
N-Nitrosodimethylamine (152)	Methylene Chloride (40) (Toluene) (111)	--
Isophorone (215)	Hydrocarbons MIBK (117) DIBK (168) Toluene (111)	Hydrocarbons TBP (289) + Hydrocarbon
2-Chlorophenol (176)	Hydrocarbons MIBK (117)	Hydrocarbons IBHK (218) TBP (289) + Hydrocarbon
bis(2-Chloroethyl)ether (178)	Hydrocarbons MIBK (117)	Hydrocarbons TBP (289) + Hydrocarbons IBHK (218)
bis(2-Chloroethoxy)-methane (218)	Hydrocarbons DIBK (168)	Hydrocarbons TBP (289) + Hydrocarbons
From I: Nitrobenzene (211)	Hydrocarbons DIBK (168)	Hydrocarbons TBP (289) + Hydrocarbons

TABLE 6-1 (Continued)

Chlorinated Hydrocarbons		Hydrocarbons	Hydrocarbons
Aromatic Hydrocarbons		Hydrocarbons	Hydrocarbons
Phenol (181)		MIBK (117) Diisopropyl Ether (68)	TOPO/diluent TBP (289)/diluent
Polyhydroxy Phenols - e.g., Resorcinol (277); Pyrocatechol (240)	MIBK (117)	TOPO/diluent (TBP (289)/diluent)	

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* - Numbers in parentheses are atmospheric boiling points, °C.

SECTION 7

CONCEPTUAL DESIGNS AND PROCESS ECONOMICS

Conceptual designs and economic analyses were carried out for several cases, including extraction of 2-chlorophenol with isobutyl heptyl ketone (IBHK - a high boiling solvent); extraction of nitrobenzene with diisobutyl ketone (DIBK - a low-boiling solvent); extraction of acrolein by methyl isobutyl ketone (MIBK), n-butyl acetate, toluene, and 1,1,2,2-tetrachloroethane (all high-boiling solvents); and extraction of acrylonitrile by methylene chloride (a low-boiling solvent) and by 1,1,2,2-tetrachloroethane (high-boiling solvent). The details of these calculations are reported by Joshi (1982) and Senetar (1982). The design and economic-analysis procedures closely paralleled those used by Ricker, et al (1980) -- see also Ricker (1978) and Ricker & King (1980). The calculations postulate 95% on-stream time.

Table 7-1 presents a breakdown of costs associated with extraction of 3000 ppm w/w of 2-chlorophenol from 11.4 m^3/h (50 gpm) of water at 30°C using IBHK. The operating costs, including fixed charges, amount to somewhat over \$4 per 1000 gallons (\$1.1/m^3) of water.

Table 7-2 presents a similar breakdown of cost components for extraction of 1000 ppm w/w of nitrobenzene from 11.4 m^3/h (50 gpm) of water at 30°C using DIBK. Two cases are considered, with and without vacuum steam stripping to recover residual DIBK from the effluent water. There is clearly a substantial incentive to recover DIBK. Even with recovery of DIBK, the cost is about 23% higher than for the extraction process for 2-chlorophenol considered in Table 7-1, because of higher steam costs to take the low-boiling solvent overhead, and because of the added charges associated with recovering DIBK, which is more soluble than IBHK, from water.

Table 7-3 summarizes the costs components for extraction of 200 ppm of acrolein from 30,000 lb/h of water by means of four different high-boiling solvents. Details of these analyses are given in Tables 7-4 through 7-7. The costs range from \$8.55 to \$13.48 per 1000 gallons of water, with 1,1,2,2-tetrachloroethane being least expensive because of low steam cost and toluene most expensive because of high capital cost. No cost penalty was imposed on the chlorinated hydrocarbon for possible extra processing to ensure full removal of it from water.

Table 7-8 summarizes cost components for extraction of 200 ppm of acrylonitrile from 125,000 lb/h of water. More detailed analyses are given in Tables 7-9 and 7-10. The high-boiling solvent, 1,1,2,2-tetrachloroethane, is less costly (\$4.10/1000 gallons of water) than the low-boiling solvent, methylene chloride (\$9.27/1000 gallons of water), primarily because of lower steam costs when the solvent does not have to be taken overhead in the regeneration column. Again no specific cost penalty has been associated with the use of the chlorinated hydrocarbons as solvents.

The bases used for the cost calculations for extractions of 2-chlorophenol and nitrobenzene are somewhat different from those used for the cost calculations for extractions of acrolein and acrylonitrile. These cover a range of conditions which might occur in different plant locations and economic situations.

TABLE 7-1. PRELIMINARY ECONOMICS FOR 2-CHLOROPHENOL EXTRACTION USING ISOBUTYL HEPTYL KETONE

Direct Costs:		
Extract-Solvent Heat Exchangers	$31,300	(29.3%)
Extractor	30,000	(28.0%)
Regenerator	24,300	(22.7%)
Reboiler	17,300	(16.2%)
Condenser	4,100	(3.8%)
Total Direct Cost	$107,000	(100%)
Indirect Costs:		
(38% of Direct Costs) $	40,700	
Fixed Capital Investment (FCI)	$ 147,700	
Fixed Charges:		
Depreciation (8% FCI) $ 11,800/yr.		
Maintenance (6% FCI) 8,900		
Insurance and Taxes (3% FCI)	4,400	
Total Fixed Charges (17% FCI)	$25,100/yr.	
Direct Operating Costs:		
Make-up Solvent	$21,400/yr.	
Utilities: 400# Steam	15,200	
Cooling Water	200	
Labor, Supervision, Lab Charges	41,300	
Total Direct Operating Costs	$78,100/yr.	
Annual Operating Cost: $103,200		

Operating Costs (per 1,000 gallons of wastewater)

Items	Cost
Labor-dependent	$1.65
Capital-dependent	1.00
Solvent	0.86
Utilities	0.62
Total Operating Cost	$4.13

TABLE 7-2. PRELIMINARY ECONOMICS FOR NITROBENZENE EXTRACTION USING DI-ISOBUTYL KETONE

	Case I No Solvent Recovery	Case II Including Steam Stripping
Direct Costs:		
Regenerator	$ 50,700 (41.0%)	$ 50,700 (30.5%)
Extract-Solvent Heat Exchanger	27,200 (22.0%)	27,200 (16.4%)
Extractor	22,100 (17.9%)	22,100 (13.3%)
Reboiler	17,500 (14.1%)	17,500 (10.5%)
Regenerator Condenser	6,200 (5.0%)	6,200 (3.7%)
Vacuum Stripper		33,000 (19.9%)
Stripper Condenser	----------	9,400 (15.7%)
Total Direct Cost	$123,700 (100%)	$166,100 (100%)
Indirect Costs: (38% of Direct Costs)	$ 47,000	$ 63,100
Fixed Capital Investment (FCI)	$170,700	$229,200
Fixed Charges:		
Depreciation (8% FCI)	$13,700/yr	$18,300/yr.
Maintenance (6% FCI)	10,200	13,800
Insurance and Taxes (3% FCI)	5,100	6,900
Total Fixed Charges (17% FCI)	$29,000/yr.	$39,000/yr.
Direct Operating Costs:		
Make-up Solvent	$ 71,400/yr.	$ 9,100/yr.
Utilities: 100# Steam	----	3,100
400# Steam	32,500	32,500
Cooling Water	1,000	2,300
Labor, Supervision, Lab Charges	41,300	41,300
Total Direct Operating	$146,200/yr.	$ 88,300/yr.
Annual Operating Cost:	$175,200/yr.	$127,300/yr.

Table 7-2 (Continued)

Operating Costs (per 1,000 gallons of wastewater)

Items	Case I No Solvent Recovery	Case II Including Steam Stripping
Labor-dependent	$1.65	$1.65
Capital-dependent	1.16	1.55
Solvent	2.86	0.37
Utilities	1.34	1.52
Total Operating Cost	$7.01	$5.09

TABLE 7-3. BREAKDOWN OF OPERATING COSTS FOR EXTRACTION OF ACROLEIN (220 ppm)

	Costs - $/1000 Gallons of Water			
Solvent	MIBK	Butyl Acetate	Tetrachloroethane	Toluene
Labor	2.477	2.477	2.477	2.477
Capital	3.054	3.223	3.756	6.347
Solvent loss	1.453	1.446	0.746	0.558
Utilities	4.109	3.747	2.079	4.605
Credit for Acrolein	(-0.511)	(-0.511)	(-0.511)	0.511)
Total	10.58	10.38	8.55	13.481

TABLE 7-4. ESTIMATION OF OPERATING COST: EXTRACTION OF ACROLEIN BY MIBK

(30,000 lb/hr WATER, 200 ppm ACROLEIN)

Item and Basis	Dollars / yr	Dollars / 1000 gallon water
Operating Labor Charges:		
1/3 operator/shift at 125,000 dollars/operator/shift	45,000	1.501
Labor Dependent Charges:		
Fringe Benefits 22% of operating labor	9,900	0.331
Supervision, Clerical, 18% of operating labor	8,100	0.270
Operating Supplies, 10% of operating labor	4,500	0.151
Laboratory, 15% of operating labor	6,750	0.225
Fixed Charges:		
Maintenance, 6% of DFC	22,890	0.764
Depreciation, 10% of DFC	38,150	1.273
Insurance, 1% of DFC	3,820	0.127
Local Taxes, 2% of DFC	7,640	0.255
Factory Expenses, 5% of DFC	19,080	0.636
Make-Up Solvent Costs:		
Loss in Regenerator	19,380	0.646
Loss in Stripper,	24,190	0.807
Utilities:		
150 psig steam, $\$ \frac{8.90}{1000\ lb}$	84,810	2.829
cooling water, and refergeration	38,390	1.280
Credit for by Product Acrolein ($\frac{1}{2}$ x market price)	(-15,320)	(-0.512)
Total Operating Cost Without Interest	317,260	10.580
Interest, 10% of DFC	38,150	1.272
Total Operating Cost With Interest	355,410	11.854

TABLE 7-5. ESTIMATION OF OPERATING COST: EXTRACTION OF ACROLEIN BY BUTYL ACETATE (30,000 lb/hr WATER, 200 ppm ACROLEIN)

Item and Basis	Dollars / yr	Dollars / 1000 gallon water
Operating Labor Charges:		
1/3 operator/shift at 125,000 dollars/operator/shift	45,000	1.501
Labor Dependent Charges:		
Fringe Benefits 22% of operating labor	9,900	0.331
Supervision, Clerical, 18% of operating labor	8,100	0.270
Operating Supplies, 10% of operating labor	4,500	0.151
Laboratory, 15% of operating labor	6,750	0.225
Fixed Charges:		
Maintenance, 6% of DFC	24,150	0.806
Depreciation, 10% of DFC	40,260	1.343
Insurance, 1% of DFC	4,030	1.134
Local Taxes, 2% of DFC	8,060	0.268
Factory Expenses, 5% of DFC	20,130	0.672
Make-Up Solvent Costs:		
Loss in Regenerator	34,200	1.141
Loss in Stripper	9,160	0.306
Utilities:		
150 psig steam, $\$ \frac{8.90}{1000\ lb}$	78,680	2.624
cooling water, and refrigeration	33,650	1.123
Credit for by Product Acrolein ($\frac{1}{2}$ x market price)	(-15,320)	(-0.511)
Total Operating Cost Without Interest	311,240	10.38
Interest, 10% of DFC	40,260	1.343
Total Operating Cost With Interest	351,500	11.724

TABLE 7-6. ESTIMATION OF OPERATING COST: EXTRACTION OF ACROLEIN BY TETRACHLOROETHANE (30,000 lb/hr WATER, 200 ppm ACROLEIN)

Item and Basis	Dollars / yr	Dollars / 1000 gallon water
Operating Labor Charges:		
1/3 operator/shift at 125,000 dollars/operator/shift	45,000	1.501
Labor Dependent Charges:		
Fringe Benefits 22% of operating labor	9,900	0.331
Supervision, Clerical, 18% of operating labor	8,100	0.270
Operating Supplies, 10% of operating labor	4,500	0.151
Laboratory, 15% of operating labor	6,750	0.225
Fixed Charges:		
Maintenance, 6% of DFC	28,150	0.939
Depreciation, 10% of DFC	46,920	1.565
Insurance, 1% of DFC	4,690	0.157
Local Taxes, 2% of DFC	9,380	0.313
Factory Expenses, 5% of DFC	23,680	0.783
Make-Up Solvent Costs:		
Loss in Regenerator	19,670	0.623
Loss in Stripper	3,880	0.123
Utilities:		
150 psig steam, $\$ \frac{8.90}{1000\ lb}$	44,130	1.398
cooling water and refrigeration	15,620	0.521
Credit for by Product Acrolein ($\frac{1}{2}$ x market price)	(-16,320)	(-0.511)
Total Operating Cost Without Interest	256,220	8.55
Interest, 10% of DFC	46,920	1.565
Total Operating Cost With Interest	303,140	10.111

TABLE 7-7. ESTIMATION OF OPERATING COST: EXTRACTION OF ACROLEIN BY TOLUENE (30,000 lb/hr WATER, 200 ppm ACROLEIN)

Item and Basis	Dollars / yr	Dollars / 1000 gallon water
Operating Labor Charges:		
1/3 operator/shift at 125,000 dollars/operator/shift	45,000	1.501
Labor Dependent Charges:		
Fringe Benefits 22% of operating labor	9,900	0.331
Supervision, Clerical, 18% of operating labor	8,100	0.270
Operating Supplies, 10% of operating labor	4,500	0.151
Laboratory, 15% of operating labor	6,750	0.225
Fixed Charges:		
Maintenance, 6% of DFC	47,580	1.587
Depreciation, 10% of DFC	79,300	2.645
Insurance, 1% of DFC	7,930	0.264
Local Taxes, 2% of DFC	15,860	0.529
Factory Expenses, 5% of DFC	39,650	1.322
Make-Up Solvent Costs:		
Loss in Regenerator	16,460	0.549
Loss in Stripper	270	0.009
Utilities:		
150 psig steam, $\$ \frac{8.90}{1000\ lb}$	93,860	3.131
cooling water and refrigeration	4,680	1.474
Credit for by Product Acrolein ($\frac{1}{2}$ x market price)	-15,320)	(-0.511)
Total Operating Cost Without Interest	404,010	13.48
Interest, 10% of DFC	79,300	2.645
Total Operating Cost With Interest	483,310	16.120

TABLE 7-8. BREAKDOWN OF OPERATING COSTS FOR EXTRACTION OF ACRYLONITRILE

(200 ppm, 125,000 lb/hr WASTEWATER

	Costs - $/1000 Gallon of Water	
	Methylene Chloride	Tetrachloroethane
Solvent:		
Labor	0.594	0.594
Capital	2.157	1.724
Solvent loss	0.591	0.520
Utilities	6.312	1.646
Credit for Acrylonitrile	(-0.379)	(-0.379)
Total	9.274	4.104

TABLE 7-9. ESTIMATION OF OPERATING COST: EXTRACTION OF ACRYLONITRILE BY METHYLENE CHLORIDE (125,000 lb/hr WATER, 200 ppm ACRYLONITRILE)

Item and Basis	Dollars / y	Dollars / 1000 gallon water
Operating Labor Charges:		
1/3 operator/shift at 125,000 dollars/operator/shift	45,000	0.360
Labor Dependent Charges:		
Fringe Benefits 22% of operating labor	9,900	0.079
Supervision, Clerical, 18% of operating labor	8,100	0.065
Operating Supplies, 10% of operating labor	4,500	0.036
Laboratory, 15% of operating labor	6,750	0.054
Fixed Charges:		
Maintenance, 6% of DFC	67,360	0.539
Depreciation, 10% of DFC	112,270	0.899
Insurance, 1% of DFC	11,230	0.090
Local Taxes, 2% of DFC	22,460	0.180
Factory Expenses, 5% of DFC	56,130	0.449
Make-Up Solvent Costs:		
Loss in Regenerator	23,820	0.191
Loss in Stripper	49,930	0.400
Utilities:		
150 psig steam, $\$ \frac{8.90}{1000\ lb}$	664,440	5.319
cooling water,	124,070	0.993
Credit for by Product Acrolein ($\frac{1}{2}$ x market price)	-47,370)	(-0.379)
Total Operating Cost Without Interest	1,158,590	9.274
Interest, 10% of DFC	112,270	0.899
Total Operating Cost With Interest	1,270,860	10.173

TABLE 7-10. ESTIMATION OF OPERATING COST: EXTRACTION OF ACRYLONITRILE BY TETRACHLOROETHANE (200 ppm ACRYLONITRILE; 125,000 lb/hr WATER)

Item and Basis	Dollars / yr	Dollars / 000 gallon water
Operating Labor Charges:		
1/3 operator/shift at 125,000 dollars/operator/shift	45,000	0.360
Labor Dependent Charges:		
Fringe Benefits 22% of operating labor	9,900	0.079
Supervision, Clerical, 18% of operating labor	8,100	0.065
Operating Supplies, 10% of operating labor	4,500	0.036
Laboratory, 15% of operating labor	6,750	0.054
Fixed Charges:		
Maintenance, 6% of DFC	53,800	0.431
Depreciation, 10% of DFC	89,600	0.718
Insurance, 1% of DFC	8,970	0.072
Local Taxes, 2% of DFC	17,930	0.144
Factory Expenses, 5% of DFC	44,830	0.359
Make-Up Solvent Costs:		
Loss in Regenerator	49,600	0.397
Loss in Stripper	15,310	0.123
Utilities:		
150 psig steam, $\$ \frac{8.90}{1000 \text{ lb}}$	193,430	1.548
cooling water, $\frac{21 \text{ cents}}{1000 \text{ gallon}}$	12,230	0.098
Credit for by Product Acrolein ($\frac{1}{2}$ x market price)	(-47,370)	(-0.379)
Total Operating Cost Without Interest	512,640	4.104
Interest, 10% of DFC	89,600	0.718
Total Operating Cost With Interest	602,300	4.822

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